Functionalisation *versus* mineralisation of some *N*-heterocyclic compounds upon UV-illumination in the presence of un-doped and iron-doped TiO₂ photocatalysts

J.A. Navío [a],*, M. Macias [a], M. Garcia-Gómez [b], M.A. Pradera [b]

[a] *Instituto de Ciencia de Materiales de Sevilla, Centro Mixto CSIC-Universidad de Sevilla and Dpto. de Química Inorgánica, Universidad de Sevilla, Avda, Américo Vespucio s/n, 41092 Sevilla, Spain*
[b] *Dpto. de Química Orgánica. Universidad de Sevilla C. Prof. García González, no. 1, 41012 Sevilla, Spain*

Abstract

Heterogeneous photocatalytic oxidation of some *N*-heterocyclic compounds (4-picoline, and 6- and 8-methylquinoline) in oxygenated solvents (water or acetonitrile), containing dispersed photocatalyst (un-doped or iron-doped titanium dioxide), was investigated under UV-illumination in a photochemical reactor. This work aimed to correlate experimental parameters such as structural aspects of the substrates, photocatalyst chemical and surface properties, illumination times, and the nature of the solvent with the extent of mineralisation of the substrates and, also, possible selective methyl group functionalisation.

Analysis of the products resulting from heterogeneous photocatalytic oxidation of 6- and 8-methylquinoline suspensions in oxygenated acetonitrile with illumination periods of <24 h detected, in both cases, the corresponding formyl derivatives quinoline-6- and -8-carbaldehyde, though at low levels. The presence of water appeared to inhibit heterogeneous photocatalytic functionalisation. However, the heterogeneous photocatalytic degradation of such compounds in water proceeds via polyhydroxylated intermediates which consequently undergo mineralisation, which, from a pollution control perspective is beneficial.

The physicochemical properties of the photocatalyst were also shown to be influential. Particularly, differences in the affinity to, and mode of adsorption of the substrate compounds studied gave rise to differences in the extent of oxidation.

Analysis of photogenerated oxidation products enabled some mechanistic insight into the course of the semiconductor-mediated reaction.

The results obtained allow a useful comparison of the functionalisation of *N*-Heterocyclic compounds via heterogeneous photocatalytic processes in the absence of water, to those carried out in the presence of water, which gave complete mineralisation.
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1. Introduction

Most N-containing molecules are anthropogenic species widely employed as pesticides, herbicides and as drugs. In particular, pyridine and its alkyl derivatives (picolines) are used as reagents in many manufacturing and industrial processes due to their complete solubility in water. Despite their widespread industrial use, the health hazards these compounds pose to humans and animals are well known. Quinolines, which are also soluble in water, are particularly hazardous. The structure–toxicity relationship of selected *N*-heterocyclic compounds has previously been reported [1]. Toxicity was found to increase linearly with molecular weight and boiling point. Both of these parameters are increased by the addition of alkyl and aryl substituents.

Quinolines and quinoline derivatives are often used in medicine (plasmocid, quinine, etc.). Quinolinecarboxaldehydes are particularly important in biomedicine due to their bactericidal, insecticidal and fungicidal properties [2].

Inhibition of corrosion of aluminium and aluminium–magnesium alloys by some *N*-heterocyclic compounds (pyridine, picolines and quinolines) has also been investigated [3].

* Corresponding author.
E-mail address: navio@us.es (J.A. Navío).

N-heterocyclic compounds, such as pyridine, picolines, quinolines and isoquinolines can be successfully extracted from aqueous streams, with or without electrolytes and at varying pH, via adsorption onto activated carbon, employing fixed bed systems [4], facilitating the practical recovery (but not elimination) of toxic heterocyclic amines from dilute aqueous waste streams.

Heterogeneous photocatalysis is an emerging technology that has been applied to air and water purification and remediation, whereby organic and inorganic pollutants in both gas and liquid phases can be degraded. The main goal of research and development in this area is the use of the technique for air purification and wastewater treatment. The main advantages are the generally mild conditions employed and the high potency for the transformation of very toxic molecules into less harmful ones [5]. The main application of heterogeneous photocatalysis (judged by the number of publications relating to the topic) is the degradation and complete mineralisation of aqueous pollutants [5,6].

Titanium dioxide, TiO_2 has been employed extensively in both fundamental and applied heterogeneous photocatalysis and it is accepted as one of the best photocatalysts [5,6]. Although TiO_2 is the most commonly used photocatalyst, metal-doped titania samples are receiving increasing attention as more efficient alternatives to bare TiO_2 [7]. In particular, iron(III)-doped TiO_2 catalyst, systems have shown much potential, with a low Fe^{3+} loading producing enhanced rates of photoreaction as a result of an improved trapping-to-recombination ratio [8].

Heterogeneous photocatalysis has been known for some time as a useful means for oxidising liquid-phase organic compounds in order to obtain either synthetically useful products [9] or to destroy organic pollutants in wastewater [5,6]. The concept of converting a pollutant, via selective oxidation, to a non-toxic, high-value chemical product is highly attractive. The application of heterogeneous photocatalysis as a synthetic transformation has been investigated, though not widely, as semiconductor photocatalytic reactions are regarded generally as highly unselective, particularly in water [9,10].

Methyl groups provide a source of structural diversity in heterocyclic chemistry. Additionally, the sunlight induced functionalisation of some heterocyclic bases in the presence of polycrystalline TiO_2 has been previously reported [11]. In spite of the recognised toxicity of several *N*-heterocyclic compounds their photo-mineralisation therefore deserves scrutiny.

The side chain functionalisation of picolines and related heterocyclic compounds is of great interest in organic synthesis. In particular, the selective transformation of methyl groups into formyl groups in methylquinolines is of great interest because the corresponding aldehydes are either very expensive or are unknown. We have previously reported a preliminary study of the photo-oxidation of 6- and 8-methylquinoline with suspended TiO_2 powder in oxygenated acetonitrile [12].

The aim of the work reported here was to study in detail functionalisation *versus* mineralisation for some *N*-heterocyclic compounds (picolines **1** and quinolines **2**), in both water and neat acetonitrile, employing un-doped and iron-doped TiO_2 as heterogeneous photocatalysts.
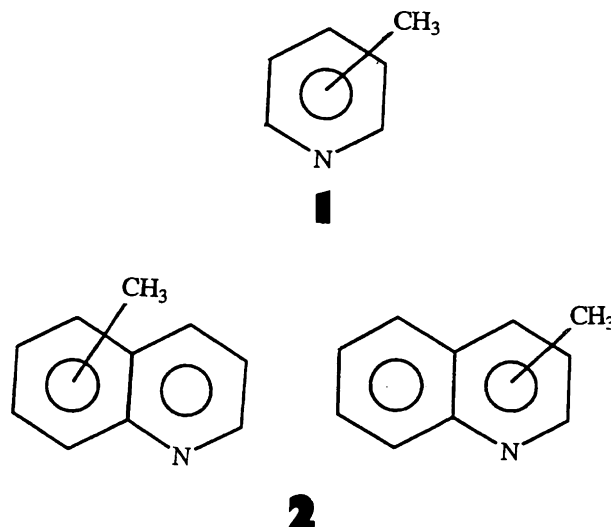
2. Experimental

Two photocatalysts were used in the study, both in powder form. Pure TiO_2 (Degussa, P25) which was previously calcined in air at 500 °C for 24 h, and iron-doped titania, Fe–TiO_2 containing Fe^{3+} at 0.5 wt.%. The latter was prepared by incipient wet impregnation of powdered TiO_2 (P25), using an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ (Merck) which contained the requisite quantity of Fe^{3+}. After standing for 48 h water was evaporated at 110 °C for 24 h and the dried solid was then fired in air at 500 °C for 24 h. The iron content was checked by atomic adsorption using a PerkinElmer 2380 spectrophotometer. Bulk and surface characterisation of the two catalysts can be found elsewhere [13].

The surface acidity (sum of Brönsted and Lewis acid sites) was measured by spectrophotometric titration [14] using pyridine ($pK_a = 5.3$) or benzoic acid ($pK_a = 4.2$) as adsorbates. BET surface areas were determined using a Micromeritics Flowsorb 2200 instrument, employing N_2 at 77 K. All chemicals used commercial products of at least reagent grade.

Photo-oxidation experiments were carried out in a Photochemical reactor obtained from Applied Photophysics Ltd. The reactor was equipped with a 400-W medium pressure mercury-arc lamp, radiating predominantly at 365–366 nm; the lamp generated over 5×10^{19} photons s^{-1} within the reaction vessel. The lamp was contained in a double-glass immersion well, through which water was passed for cooling. A borosilicate glass sleeve was used to remove short wavelength radiation (less than 300 nm). A gas inlet reaction flask (400 mL) was used, to which a double surface condenser was fitted to prevent "creep" and loss of vapour.

In all of the experiments, the same substrate concentration (0.175 M) was used. Suspended in the solvent (350 mL of bidistilled water or pure acetonitrile) was the powdered catalyst (2.5 g L^{-1}) and pure oxygen was bubbled through the photoreactor flask. The oxygen gas was dried by passing it through a calcium chloride drying tube. Aliquots were taken from the photoreactor at fixed time intervals during the

illumination. Catalyst was separated from the samples by centrifugation and the liquid phase then analysed. Product analysis was by GC–MS, using a Kratos-MS 80RFA fitted to a Carlo Erba GC. Separations were carried out with a CP-SIL 5CBWCOT (25 m × 0.32 mm) column whose temperature was programmed from 30 °C (10 min) up to (a) 150 °C (2 min) for 6-methylquinoline or (b) 220 °C (5 min) for both 8-methylquinoline and 4-picoline, at 10 °C min^{-1}. Compound identification was based on the GC–MS data. Semi-quantitative determinations were performed using the GC profiles against an internal standard, quinoline. However, for a better identification and characterisation of reagents and products ^{13}C NMR, ^{1}H NMR and IR were used when it was required. Concentrations of NO_2^-, NO_3^- and NH_4^+ were determined by ionic chromatography (IC), using a Metrohm 690 ion chromatograph. For the anions a Hamilton anion column PRP-X100 with a phthalic acid solution, containing acetone, of pH 5 as the mobile phase was used. For NH_4^+ analysis, a Waters IC-Pack column was employed, with 2 mM nitric acid as the mobile phase. Errors in the determination of ion concentrations were less than 5%. Qualitative evidence of CO_2 evolution was obtained by bubbling through aqueous $Ba(OH)_2$.

3. Results and discussion

3.1. Bulk and surface properties of the photocatalysts

The distributions of acidic and basic sites on the un-doped and iron-doped titanium catalysts, as well as other properties, are given in Table 1. Notably, iron-doped titanium was found to possess lower levels of acidic and basic hydroxyl groups than undoped TiO_2. Without thermal pre-treatment, commercial TiO_2 Degussa P25 has been shown to be 80% anatase and 20% rutile; however, the anatase/rutile ratio is strongly dependent on the history of the sample. The anatase fraction X_A of our starting sample of TiO_2 was found to be less than 80% [13]. After calcination treatment, the initial A/R ratio of the TiO_2 decreases because the anatase to rutile transformation is less effective after prolonged calcination treatments (24 h), even at 500 °C. In fact a decrease in the anatase/rutile ratio is observed (A/R = 0.57) when the original sample is calcined at 500 °C for 24 h. As previously reported [13], Fe–TiO_2 systems have lower A/R ratios and this is apparent for the iron-doped titania in Table 1. The data presented in Table 1 will subsequently be used in the discussion of the photocatalytic oxidation results.

3.2. Blank dark- and photo-chemical experiments

Before studying the heterogeneous photocatalytic oxidation of 4-picoline, and 6- and 8-methylquinolines, blank dark- and photo-oxidation experiments were performed in neat acetonitrile media.

Several types of interaction between substrate–oxygen pair S–O_2 could be considered possible:

(a) S + O_2 (ground-state triplet oxygen)
(b) S + $^1O_2$ (singlet oxygen)
(c) S + O_2^- (superoxide ion)
(d) S^+ + O_2 (ground-state triplet oxygen)
(e) S^+ + O_2^- (superoxide ion).

Dark experiments were performed by bubbling oxygen through acetonitrile solutions of the substrate (either 4-picoline, or 6- or 8-methylquinoline) for 1 h. In all cases no products other than the initial substrate were detected.

As a result of their heteroatomic rings, pyridine, quinolines and their derivative molecules have non-bonding electrons which can make $n \rightarrow \pi^*$-type transitions besides just $\pi \rightarrow \pi^*$ [15]. Thus, prior to performing the heterogeneous photo-catalytic reactions, blank photochemical experiments were performed in order to investigate the effect of illumination on oxygen saturated solutions of 4-picoline and 6- and 8-methylquinolines in neat acetonitrile. In the absence of catalyst, even after prolonged illumination times (24 h), no photo-oxygenation products were detected for the 4-picoline and 6-methylquinoline substrates. For 8-methylquinoline only insignificant traces of quinoline-8-carbaldehyde 3 (see below) were detected. There is a plausible explanation for the formation of the quinoline-8-carbaldehyde (by-product 3) photo-oxygenation product (albeit in insignificant trace amounts) in the blank photochemical experiment. The UV absorption spectra of 8-methylquinoline shows small absorption bands around 300 nm (data not shown) and a photo-chemical oxidation could therefore be initiated by the small number of photons generated by our lamp in this range of wavelengths. For experiments carried out in darkness, in the presence of either of the catalysts, no products were detected for 4-picoline, or either 6- or 8-methylquinoline.

The results obtained from the uncatalysed photochemical and dark experiments allow the exclusion of an S + O_2 mode of interaction.

Rose Bengal is used in synthetic chemistry to generate singlet oxygen ($^1O_2$) from triplet oxygen. Photosensitised experiments

Table 1
Some properties of the un-doped and iron-doped TiO_2 catalysts

Type of catalyst	BET surface area (m^2 g^{-1})	Particle size (μm)	Acidity (μm g^{-1})	Basicity (μm g^{-1})	Anatase/rutile (A/R) ratio
TiO_2 (P25)	46.5	0.03	5.8	13.8	0.57
Fe/TiO_2 (0.5 wt.%Fe)	29.2	5[a] + 50[b]	3.4	4.3	0.45

[a] Pure TiO_2 particles.
[b] Aggregates containing iron.

Table 2
Main photogenerated products from the heterogeneous photocatalytic oxidation of 4-picoline (initial amount = 61.25 mmol)

Catalyst and solvent	Illumination time (2 h)/photogenerated products (mmol)	Illumination time (24 h) photogenerated products (mmol)
TiO$_2$ on pure CH$_3$CN	NH$_4^+$/0.85, NO$_3^-$/1.20, qualitative evidence of CO$_2$	NH$_4^+$/1.72, NO$_3^-$/2.48, qualitative evidence of CO$_2$
TiO$_2$ on water	NH$_4^+$/22.8, NO$_3^-$/37.1, qualitative evidence of CO$_2$	Not monitored
Fe–TiO$_2$ (0.5 wt.%Fe), on pure CH$_3$CN	NH$_4^+$/1.15, NO$_3^-$/1.90, qualitative evidence of CO$_2$	NH$_4^+$/2.45, NO$_3^-$/5.87, qualitative evidence of CO$_2$
Fe–TiO$_2$ (0.5 wt.%Fe), on water	NH$_4^+$/23.1, NO$_3^-$/38.2, qualitative evidence of CO$_2$	Not monitored

were thus performed by bubbling oxygen through Rose Bengal in acetonitrile solutions of the substrates (4-picoline, and 6- and 8-methylquinoline). No products were ever detected even after illumination for 8 h. As no reaction was therefore occurring via photosensitised electron transfer, an S + ^{1}O$_2$ mode of interaction can also be excluded.

Furthermore, we observed that none of the substrates underwent any reaction with dissolved potassium superoxide, even upon stirring for periods comparable to the irradiation periods used and as a result an S + O$_2^-$ mode of interaction can also be excluded. At this stage the S + O$_2$ and S$^+$ + O$_2^-$ modes of interaction thus remain as possible.

3.3. Heterogeneous photocatalytic oxidation of picolines

The heterogeneous photocatalytic oxidation of 4-picoline in both bidistilled water and neat acetonitrile was studied for both of the catalysts: un-doped TiO$_2$ and Fe–TiO$_2$ (0.5 wt.%Fe). No partial oxidation products were found at either short (1–2 h) or prolonged illumination times (24 h) using either catalyst in pure water or acetonitrile. However, evidence of the progressive formation of CO$_2$, NH$_4^+$ and NO$_3^-$ was detected during the course of illumination. NO$_2^-$ species were not detected (Table 2). The formation of these species was more extensive for the iron-doped titanium catalyst than for the undoped TiO$_2$ and also proceeded more rapidly in water than in acetonitrile, the substrate persisting in the latter even after prolonged times of illumination (24 h). Total decomposition of 4-picoline was observed for both catalysts after 2 h of illumination in water, the final ratio of NH$^+$/NO$_3^-$ was approximately 0.60. The concentration–time profiles of these compounds were not monitored; however a mass balance for nitrogen can be used to estimate the percentage mineralisation of 4-picoline. As shown in Table 3 practically total mineralisation of 4-picolines was observed after 2 h of illumination for both of the catalysts in water. Since mineralisation occurs so quickly for both catalysts in water, comparison of the two photocatalysts in water is therefore very difficult in any case. Since reduction of the

nitrogen atom in the substrate is unlikely under the oxidising conditions, we would suggest that rupture of the ring system in 4-picoline occurs, forming ammonium ions which undergo further photocatalytic oxidation to NO$_3^-$.

The absence of selectivity for both un-doped and iron-doped TiO$_2$ photocatalysed oxidation of 4-picoline, in comparison with results obtained for the same system employing toluene as substrate [16], where partial oxidation products were observed, may be due to relatively strong adsorption of the nitrogen atom, which prevents desorption of partly oxidised intermediates (if any). Our results apparently partly conflict with those reported by Fox [17] for the TiO$_2$-photocatalysed oxidation of 2-picoline, where partial oxidation products were observed during the photoreaction.

In trying to explain the results here, several points should be taken into account. A stronger adsorption of picolines, in a vertical orientation, via the nitrogen atom is expected. Because recombination of the photogenerated electron and resultant hole is so rapid, interfacial electron transfer is a kinetically competitive process only when the donor or acceptor is preadsorbed onto the catalyst surface. Indeed, it has been suggested that strong preliminary adsorption is prerequisite for efficient mineralisation. Evidently, adsorption, via a nitrogen atom, of the substrate to the catalyst surface, forming a surface complex, may be necessary in the formation of NH$_4^+$/NO$_3^-$ ions. Steric hindrance around the nitrogen heteroatom in 2-picoline may result in a lesser capacity for adsorption of this molecule compared to 4-picoline. This being the case, partial oxidation products in the heterogeneous photocatalytic oxidation of 2-picoline might be expected, as observed by Fox et al. [17]. It is known that benzene and its derivatives (i.e. toluene) can form a variety of charge transfer complexes depending on their electron-donating or electron-accepting capacity [18]. The interaction of benzene with the surface of TiO$_2$ has been studied by Suda [19,20]. This work concluded that (-electron rich benzene is adsorbed in a flat orientation onto a dehydroxylated site, preferentially by surface Ti^{4+} ions, through the formation of charge-transfer complexes. A weakly reversible adsorption

Table 3
Percentage of mineralisation for the heterogeneous photocatalytic oxidation of 4-picoline in either water or acetonitrile

Illumination time (h)	TiO$_2$ on pure CH$_3$CN (%)	TiO$_2$ on water (%)	Fe-TiO$_2$ (0.5 wt.%Fe) on pure CH$_3$CN (%)	Fe-TiO$_2$ (0.5 wt.%Fe) on water (%)
2	3.4	97.8	5.0	100
24	6.8	–	13.6	–

of benzene onto the hydroxylated surface was also reported via OH···π interactions. Similar results have been reported for the interaction of toluene molecules with titanium catalysts [20], and this type of interaction would facilitate close proximity of the toluene methyl group to the catalyst surface and consequently its photo-oxidation. However, for 4-picoline, a stronger, vertically orientated adsorption via the nitrogen atom is expected and, as previously stated, this may be necessary for mineralisation via the formation of NH_4^+/NO_3^- ions.

The fact that both the un-doped and iron-doped titanium samples showed virtually the same photocatalytic activity indicates that differences in surface acidity and anatase/rutile ratios between the two catalysts (Table 1) are practically negligible. This is probably because of the opposing effects of higher adsorption capacity (greater in TiO_2) compared to higher charge transfer capacity (greater in the iron-doped titanium sample).

Finally, some extent of mineralisation was observed in the heterogeneous photocatalytic oxidation of the 4-picoline in oxygenated acetonitrile (Tables 2 and 3). Although neat liquid acetonitrile was used in this work, the progressive formation of CO_2 as well as the NH_4^+/NO_3^- species could be attributed to the action, and thus presence, of water. We hypothesise that mineralisation might be initiated by the low amount of surface-bound hydroxyl radicals, as in our experimental systems, the photocatalysts were not dehydrated before use. Indeed, after prolonged illumination qualitative evidence of carbon dioxide evolution, together with a slight increase in the amount of NH_4^+/NO_3^- was observed. The simultaneous production of water would thus allow the continual generation of hydroxyl radicals.

3.4. Heterogeneous photocatalytic oxidation of quinolines

Heterogeneous photocatalytic oxidations of two selected quinolines (6- and 8-methylquinoline) in both bidistilled water and neat acetonitrile, and employing both un-doped TiO_2 and Fe-TiO_2 (0.5 wt.%Fe) catalysts were also studied, in experimental conditions analogous to those used in the 4-picoline oxidations.

Several oxidation products were observed (Table 4) for these reactions, indicating that both UV-illumination and the presence of the catalysts are essential. With each reaction employing equal conditions, three factors were found to affect the selectivity of the photoproducts: the illumination time, the nature of the photocatalyst and the position of the methyl subsistent on the substrate. For the two substrates, 6- and 8-methylquinoline, the main oxidation products produced were quinoline-6-carbaldehyde **3** or quinoline-8-carbaldehyde **4** respectively, although for the latter quinoline-8-carboxylic acid **5** was also detected at similar levels to the aldehyde, depending on the illumination time. The quantification of the products reported in Table 4 is rather tenuous since percentage areas of the chromatographic peaks are used, but the different compounds would likely have varying sensitivities to the column employed. The proportionality of the peak areas for reagents and products in each of these experiments should therefore be considered only a semi-quantitative analysis. Most of the products, including the corresponding aldehydes that were detected here are unknown.
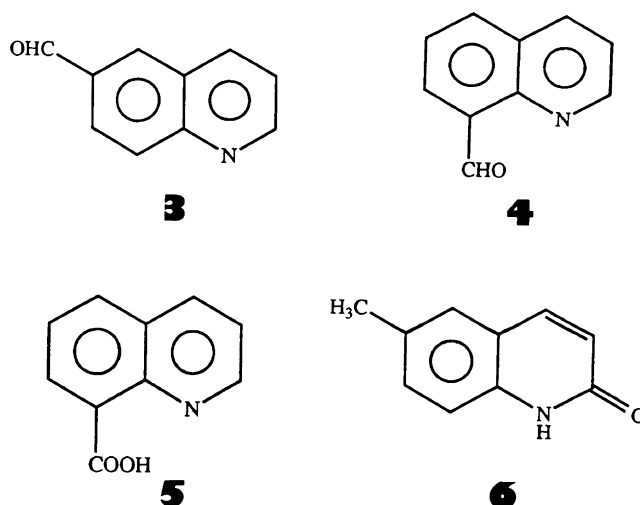

3 **4** **5** **6**

Table 4

Main photogenerated products for the heterogeneous photocatalytic oxidation of 6- and 8-methylquinolines in acetonitrile solvent; (initial amounts of substrates = 61.25 mmol)

Substrate and catalyst	Reagent and products	Illumination time (h)	Area of the chromatographic peak (%)[a]
6-Methylquinoline on TiO_2	6-Methylquinoline	144	60
	Quinoline-6-carbaldehyde (**3**)	144	2.53
	6-Methylquinolin-2(1H)-one (**6**)	144	2.45
8-Methylquinoline on TiO_2	8-Methylquinoline	24	148
		144	103
	Quinoline-8-carbaldehyde (**4**)	24	2.49
		144	2.78
	Quinoline-8-carboxylic acid (**5**)	144	2.45
6-Methylquinoline Fe–TiO_2 (0.5 wt.%Fe)	6-Methylquinoline	24	129
	Quinoline-6-carbaldehyde (**3**)	24	0.57
8-Methylquinoline Fe–TiO_2 (0.5 wt.%Fe)	8-Methyilquinoline	5	151
		24	132
	Quinoline-8-carbaldehyde (**4**)	5	0.89
		24	3.80
	Quinoline-8-carboxylic acid (**5**)	24	7.17

[a] Percentage referred to the area of the chromatographic peak of the substance used as internal reference (quinoline).

For 6-methylquinoline, an illumination time of <24 h in the presence of TiO$_2$, produced only trace levels of quinoline-6-carbaldehyde **3**, the sole product. However, a prolonged illumination period produced resulted in an increase in the amount of this aldehyde and the simultaneous appearance of 6-methylquinolin-2(1*H*)-one **6**, these two compounds comprising the main products. The presence of the latter product indicates that de-aromatisation and subsequent oxidation of the N-atom ring of 6-methylquinoline occurred. It is hypothesised that the formation of **6** can be attributed to a mechanism of photo-oxidation for 6-methylquinoline which goes via the quinolinium cation **7**, formed when the quinoline is adsorbed to the Brönsted acidic sites of the catalyst (Scheme 1). Further attack by the superoxide species O$_2^-$ on the 6-methylquinolinium generates the intermediate 6-methyl-1,2-dihydroquinolinylperoxyl radical, **8**, which can then undergo dehydroxylation, facilitated by Brönsted acidic sites, to yield the corresponding product **6**. If this mechanism is assumed to be correct, the lack of such a product for 8-methylquinoline (see below) can be explained by the steric effect of the 8-methyl group.

With 8-methylquinoline as substrate, an illumination period of <24 h using TiO$_2$ as catalyst yielded a significant amount of quinoline-8-carbaldehyde **4**, the only significant reaction product at this point. The concentration of carbaldehyde observed here after just 24 h was similar to that observed for the oxidation of 6-methylquinoline after a very prolonged illumination time (144 h), the higher chemical yield indicating higher selectivity in aldehyde formation for 8-methylquinoline with respect to 6-methylquinoline. However, the yield of quinoline-8-carbaldehyde after long illumination times (>24 h) remained almost constant indicating that this product subsequently undergoes further transformations under the photocatalytic conditions. The formation of significant amounts of quinoline-8-carboxylic acid **5** after an illumination period of >24 h for this reaction is clear evidence of this. In contrast, quinoline-6-carboxylic acid was not detected during the TiO$_2$-photocatalytic oxidation of 6-methylquinoline. This difference likely results from the different positions of the methyl substituents in the respective products.

The proximity of the methyl group to the nitrogen atom in 8-methylquinoline likely results in its being closer to the catalyst surface when the substrate is adsorbed to the surface, via a nitrogen–Lewis interaction with Lewis acid surface sites.

In reactions employing the iron-doped titanium catalyst, a similar distribution of products (Table 4) to those obtained using undoped TiO$_2$ was observed for both of the quinoline substrates, though higher chemical yields were observed for the iron-doped catalyst. The results are comparable to those observed for the photocatalysed oxidation of neat toluene using un-doped or iron-doped titanium catalysts [16].

Table 4 shows that for the 8-methylquinoline substrate, a prolonged illumination time (144 h) gave quinoline-8-carbaldehyde/quinoline-8-carboxylic acid in a ratio of around 1.1, when undoped TiO$_2$ was used as catalyst. However, for the iron-doped titanium catalyst this ratio was 0.5 after only 24 h of illumination. In contrast, for 6-methylquinoline after 24 h of illumination practically no change in the high selectivity for quinoline-6-carbaldehyde product was observed using either catalyst, although yield of the aldehyde was higher when the Fe–TiO$_2$ catalyst was used.

When heterogeneous photocatalytic oxidation of either 6- or 8-methylquinoline was attempted in acetonitrile, even prolonged illumination resulted in only qualitative evidence of carbon dioxide together with a slight increase in the trace amounts of NH$_4^+$/NO$_3^-$ ions observed, clear evidence of resistance to mineralisation for both quinolines in pure acetonitrile.

The results clearly demonstrate that changing the photocatalyst, with the subsequent change in the nature and number adsorption sites, affects the adsorption equilibrium, which should also affect the selectivity. One might thus expect that a methyl substituent in the 8-position on a quinoline would hinder its adsorption (if adsorption is to occur via the nitrogen atom). However, in spite of the lesser adsorption for 8-methylquinoline, the close proximity of the 8-methyl group to the catalyst surface facilitates easier oxidation. This would help explain the greater yield of aldehyde observed for the 8-methyl over the 6-
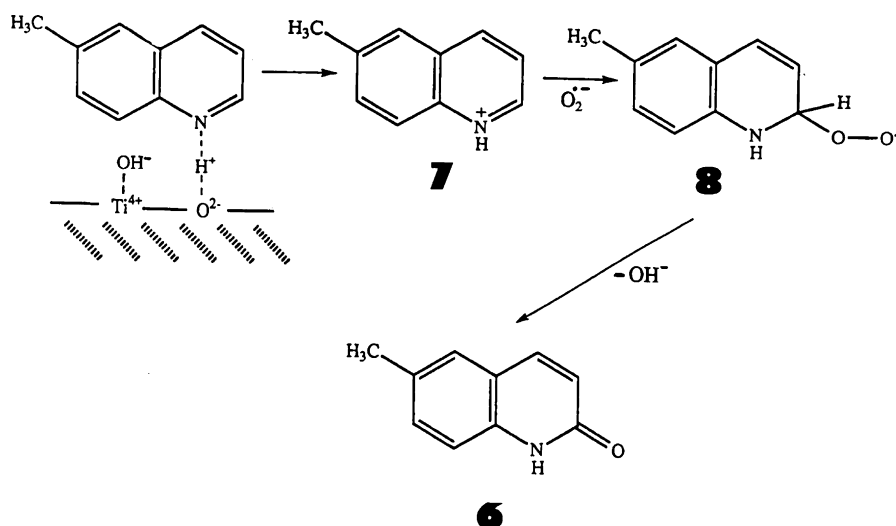
Scheme 1.

methyl substrate after illumination times of <24 h. For this same reason, further photocatalytic oxidation of the aldehyde group to the corresponding acid is more favoured for the 8-methyl rather than 6-methyl quinoline. Experimentally a progressive increase in the yield of the quinoline-8-carboxylic acid **5** over the course of illumination was observed, whilst quinoline-6-carboxylic acid **5** was never detected even after a prolonged illumination time (>24 h) which supports this theory. These differences suggest that formation of quinoline-8-carboxylic acid occurs via heterogeneous photocatalytic oxidation of quinoline-8-carbaldehyde **4**, rather than via auto-oxidation. Doping of the TiO_2 with Fe^{3+} (≈0.5 wt.%) leads to a slight diminution in the number of acid sites on the surface and an increase in the number of basic sites (see Table 1). This should result in a lesser capacity to adsorb quinoline-8-carbaldehyde **4** and a higher capacity to adsorb quinoline-8-carboxylic acid **5** (once formed). As the catalyst surfaces exhibit both acid and base properties (Table 1), it is reasonable to propose that photogenerated quinolinine-8-carboxylic acid molecules are stabilised on the surface of the catalyst via acid–base interaction. In this case, this interaction would be favoured on the surface of un-doped titanium, which exhibits higher basicity than the iron-doped titanium.

Table 5 reports results for the photocatalytic oxidations of 6- and 8-methylquinoline in water, employing both of the photocatalysts. In all cases, after short illumination periods (1–2 h), hydroxylated and polyhydroxylated methylquinoline derivatives were observed in trace amounts; for example, in the oxidation of 6-methylquinoline by both un-doped and iron-doped titanium, traces of pyridine-3-carboxylic acid **9** and tri-hydroxy-6-methylquinoline **10** were detected. A nitrogen mass balance indicated practically total mineralisation of both methylquinolines after 5 h of illumination in water for both catalysts. However, for both methylquinolines in water, as shown in Table 6, Fe–TiO_2 (0.5 wt.%Fe) is clearly a slightly more effective photocatalyst than un-doped TiO_2. As previously discussed, the presence of both NH_4^+ and NO_3^- seems to indicate that rupture of the ring system occurs for both methylquinolines, liberating ammonium ions which subsequently undergo further photocatalytic oxidation into NO_3^-, in the same manner as was suggested for the 4-picoline photodegradation.

Table 6

Percentage of mineralisation for the heterogeneous photocatalytic oxidation of 6- and 8-methylquinoline in water after 2 h of illumination

6-Methylquinoline on TiO_2	16.4%
8-Methylquinoline on TiO_2	23.3%
6-Methylquinoline Fe–TiO_2 (0.5 wt.%Fe)	26.8%
8-Methylquinoline Fe–TiO_2 (0.5 wt.%Fe)	28.8%

9 **10**
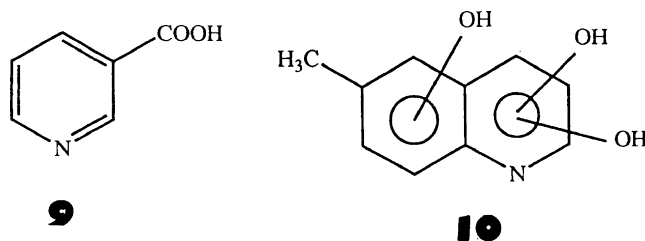
The formation of the hydroxylated methylquinolines can be explained by the presence of hydroxyl radicals from water. The hydroxyl radical is an extremely reactive species that has been used for hydroxylation of the aromatic ring alkylbenzenes [21–23]. Hydroxyl radicals photogenerated from water can be attached to the aromatic rings of methylquinolines leading to the formation of intermediate radicals that are then further de-aromatised, thus, the oxidation of carbon atoms to CO_2 is relatively easy. Herrmann et al. [9c] found that de-aromatisation is rapid even when deactivating substituents are present on the aromatic ring. On this basis, taking into account the molecular structures of 6- and 8-methylquinoline, and the prior observation that TiO_2 photocatalysis of 1-methylnaphtalene proceeds via oxidative cleavage of the methyl activated ring [9a], de-aromatisation and oxidative cleavage of the methyl activated ring in methylquinolines would be expected. The detection of pyridine-3-carboxylic acid **9** as a partial oxidation product for 6-methylquinoline indicates that this does occur. As mentioned before, de-aromatisation and subsequent oxidation is also observed in the N-atom ring of 6-methylquinoline, the formation of **6** being proof of this.

It is known that, in the presence of water, several types of oxygen-derived free radicals are formed [9] by the action of which most organic molecules are mineralised. Photocatalytic oxidation of the aromatic ring to CO_2 under UV-illumination in an aqueous emulsion of TiO_2 has been observed by Izumi et al. [24].

Table 5

Reagent and products detected for the heterogeneous photocatalytic oxidation of 6- and 8-methylquinolines in water; (initial amounts of substrates = 61.25 mmol)

Substrate and catalyst	Illumination time (2 h)/reagent[a] and inorganic photogenerated products (mmol)	Illumination time (5 h) reagent[a] and inorganic photogenerated products (mmol)
6-Methylquinoline on TiO_2	6-Methylquinoline (145%), NH_4^+/4.80, NO_3^-/5.25, qualitative evidence of CO_2	6-Methylquinoline (0.37%), NH_4^+/4.3, NO_3^-/57.2, qualitative evidence of CO_2
8-Methylquinoline on TiO_2	8-Methylquinoline (130%), NH_4^+/5.70, NO_3^-/8.58, qualitative evidence of CO_2	8-Methylquinoline (0.26%), NH_4^+/3.2, NO_3^-/58.0, qualitative evidence of CO_2
6-Methylquinoline, Fe–TiO_2 (0.5 wt.%Fe)	6-Methylquinoline (120%), NH_4^+/5.82, NO_3^-/10.58, qualitative evidence of CO_2	6-Methylquinoline (0.07%), NH_4^+/1.3, NO_3^-/59.0, qualitative evidence of CO_2
8-Methylquinoline, Fe-TiO_2 (0.5 wt.%Fe)	8-Methylquinoline (103%), NH_4^+/5.93, NO_3^-/11.68, qualitative evidence of CO_2	8-Methylquinoline (0.05%), NH_4^+/traces, NO_3^-/61.1, qualitative evidence of CO_2

[a] Percentage referred to the area of the chromatographic peak of the substance used as internal reference (quinoline).

Although this study is not a deep mechanistic investigation, it should be noted that according to the results in Section 3.2 the interaction modes $S + O_2$, $S + {}^1O_2$ and $S + O_2^-$ can be discarded. The $S^+ + O_2$ and $S^+ + O_2^-$ modes of interaction thus remain as possible routes for the heterogeneous photocatalytic oxidation of 4-picoline, and 6- and 8-methylquinoline, probably via a mechanism involving radical cation RN^+ isomers [25]. Independently that some authors have proposed that the superoxide species O_2^- is active for mineralisation whilst O^- is responsible for partial oxidations (functionalisation) [26], however the formation of product **6** has been explained by us invoking the superoxide radical anions O_2^-.

4. Conclusions

In conclusion, study of the photogenerated products from heterogeneous photocatalytic oxidation of the substrates, 4-picoline, and 6- and 8-methylquinoline, in oxygenated neat acetonitrile or bidistilled water containing suspended TiO_2 or iron doped TiO_2 catalyst, indicated that different factors influence the likelihood of functionalisation *versus* mineralisation of these *N*-heterocyclic compounds, not just the position of the methyl substituent on the *N*-heterocyclic ring but also the nature of the solvent. The presence of water seems to be detrimental to functionalisation whilst degradation of such compounds in water probably proceeds via polyhydroxylated intermediates, which undergo further degradation leading to mineralisation.

The nature and physicochemical properties of the photocatalyst were also found to be important. The photocatalysts capacities for adsorption were found to play an important role. Differences in the affinity and mode of adsorption for the different chemical compounds (i.e. picolines and methyl substituted quinolines) give rise to differences in their partial or complete heterogeneous photocatalytic oxidations.

FTIR studies of the interaction modes of substrates at the catalyst surface are currently in progress.

Acknowledgements

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